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Ethylcellulose-coated polyolefin separators for lithium-ion batteries with improved safety performance

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ABSTRACT

With the widely use in portable electronic devices and electric vehicles, the safety of lithium-ion battery has raised serious concerns, in which the thermal stability of separator plays an essential role in preventing thermal runaway reactions. The novelty of this work is to coat commercialized polyethylene (PE) separator and trilayer polypropylene/polyethylene/polypropylene (PP/PE/PP) separator with ethylcellulose (EC), a thermally stable and renewable biomass. The formation of the EC layer with high porosity is through a simple dipping and extracting process. The effects of the EC layer on thermal shrinkage, electrolyte wettability and cell performance are investigated. After coating, the thermal shrinkage of PE separator at shutdown and meltdown point is reduced from 20% to 9% and 42% to 23% respectively, while the drop of OCV under increasing temperature is also postponed from 130 °C to 160 °C. The electrolyte wettability of pristine trilayer PP/PE/PP separator is greatly improved, leading to increased capacity retention from 28% to 99% of the cell.

1. Introduction

The rapid depletion of fossil fuels has motivated intensive efforts to meet the increasing demands for clean energy sources. Among the various alternative power sources, lithium-ion batteries have been drawing considerable attention due to their high energy density and long cycle life (Goodenough & Park, 2013). However, reports of occasional incidents have raised serious concerns over their safety. The thermal runaway of batteries occurs at a high temperature under conditions of heating, crushing, or short-circuits and often results in a fire or even explosion (Jhu, Wang, Wen, & Shu, 2012). Various approaches have been adopted to solve this problem, such as pressure release valves, one-shot fuses, shutdown separators, chemical shuttles, non-flammable electrolytes and coatings (Balakrishnan, Ramesh, & Kumar, 2006). Among all of these mechanisms, separator is the vital element in avoiding the catastrophic thermal runaway, for its function is to avoid contact between electrodes, while allowing the lithium ions to pass through freely. If it shrink or break under increasing temperature, the internal short-circuit would happen and cause an accident.

Currently widely used separators in lithium-ion batteries are typically manufactured from polyolefins, predominantly polyethylene (PE) or polypropylene (PP), which have advantages of high tensile strength and shutdown at elevated temperature but are poor in thermal shrinkage and electrolyte wettability (Cho, Park, Kim, & Lee, 2011). Conventional dry or wet process employs a stretching step to form the open porous structures. Therefore, the membranes tend to shrink at elevated temperatures due to the polymer shape memory effect increasing the risk of battery internal shorting (Huang, 2012). In addition, their hydrophobic surface character and low surface energies result in a poor compatibility with conventional liquid electrolytes, which makes them hard to absorb and retain the liquid electrolyte, and consequently damage the cycle performance of batteries.

Many efforts have been taken to overcome the limitation of polyolefin separators. One method is to replace the polyolefins with other thermal stable materials, including non-wovens (Hao et al., 2013; Miao, Zhu, Hou, Xia, & Liu, 2013; Zhang et al., 2013; Zhu et al., 2013) and fibers(Chun et al., 2012; Huang & Hitt, 2013). However, these separators cannot inhibit the thermal runaway of batteries for not having the function of thermal shutdown as polyolefin separators. Another way is to coat the polyolefin separators by solution and grafting processes. The coated layer can be composed by inorganic nanoparticles(Fu, Luan, Argue, Bureau, & Davidson, 2012; Jung et al., 2012; Liao et al., 2011) or organic polymers(Li et al., 2011; Liu, Li, Zuo, Liu, & Li, 2013; Ryou, Lee, Park, & Choi, 2011; Song & Kim, 2010). While improving the thermal stability and electrolyte wettability of polyolefin separators, the inorganic nanoparticles require some suitable binders to stick on the surface and the ceramic layers oftentimes cannot withstand the mechanical stresses experienced during assembly and operation of the battery (Fang et al., 2011). For organic layers, some environmentally harmful or expensive chemicals are introduced and might cause other problems.

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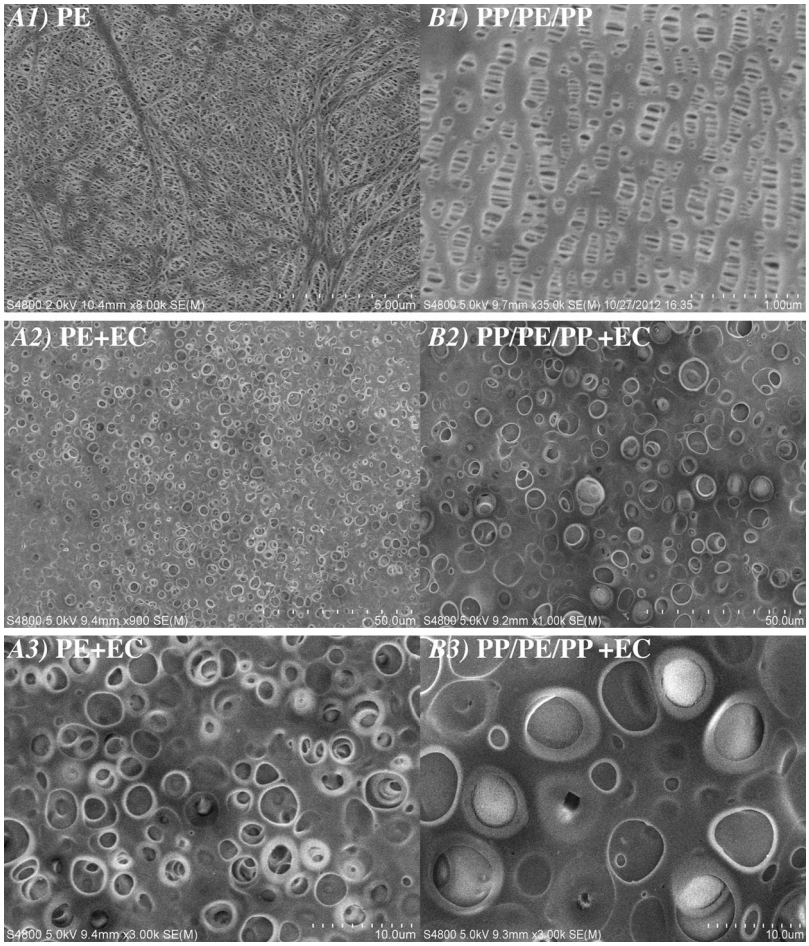


Fig. 1. FE-SEM photographs for separators: (A1) PE separator; (A2)–(A3) PE + EC coated separator; (B1) PP/PE/PP separator; (B2)–(B3) PP/PE/PP + EC coated separator.

Ethylcellulose, as derivatives of cellulose, maintain the properties of high thermal stability and polarity. However, compared to the insolubility of cellulose, it can be easily dissolved in ethanol which is crucial to the coating process because the polyolefin separators can be easily wetted by this ethanol solution, facilitating a uniform impregnation. After coating and extracting the pore-forming agents, a porous and thin ethylcellulose layer with the thickness of 2–3 μm is formed on the surface of it. Coated polyolefin separators exhibited remarkably decreased thermal shrinkage and improved electrolyte wettability, while not sacrificing the original advantages of thermal shutdown and high mechanical strength. In addition, ethylcellulose has been widely used as pharmaceutic adjuvant for its nontoxic property and can be easily fabricated with plants and wood, making this EC coating process more economical and environmentally friendly compared to the aforementioned coating processes (Muschert et al., 2009).

2. Experimental

2.1. Preparation of composite separators

Ethylcellulose (EC) (Chemically Pure, Aladdin, China), Polyvinylpyrrolidone (PVP) with an average molecular weight of 8000 (K16-18, Aladdin, China), commercialized PE separator (thickness = 22 μm, porosity = 40%, W-SCOPE) made by wet process and trilayer PP/PE/PP separator (thickness = 25 μm, porosity = 43%, UBE) made by dry stretch process, other solvents were reagent grade and used as received.

To prepare the casting solution, 3.6 g of EC were dissolved in a 120 ml mixture of ethanol and water with the volume ratio of 5–1 to form a 3% solution. In the EC solution, the same weight of PVP was added as pore-forming agents under vigorous stirring at 60 °C for 12 h.

The coating of polyolefin separators was performed with an immersion method. The polyolefin separator was first mounted on 10 cm × 10 cm plastic frame and then was immersed into the casting solution in a Petri dish. The Petri dish was sealed at 30 °C for 30 min for impregnation. Then the impregnated separator was dried at 90 °C in a vacuum oven for 1 h to remove the organic solvents. The casted separator was immersed in a pool of deionized water for 24 h to remove the PVP from EC and generated porous structure. The separator was then dried at ambient temperature.

2.2. Characterization of the coated separators

2.2.1. Morphology of the separators

The morphologies of separators were observed using a field emission scanning electron microscope (FE-SEM, S-4800, Hitachi).

2.2.2. Thermo shrinkage and OCV test

DSC and TGA scans were performed with a simultaneous TG-DSC system (STA 449F3, NETZSCH) at the rate of 5 °C min^{-1} under nitrogen purge from 30 °C to 350 °C. TMA tests were performed on a TMA analyzer (TMA202, NETZSCH) under N2 atmosphere and the temperature was increased from 30 °C to 200 °C at the rate of 5 °C min^{-1}, with a constant external tensile force of 0.02 N.

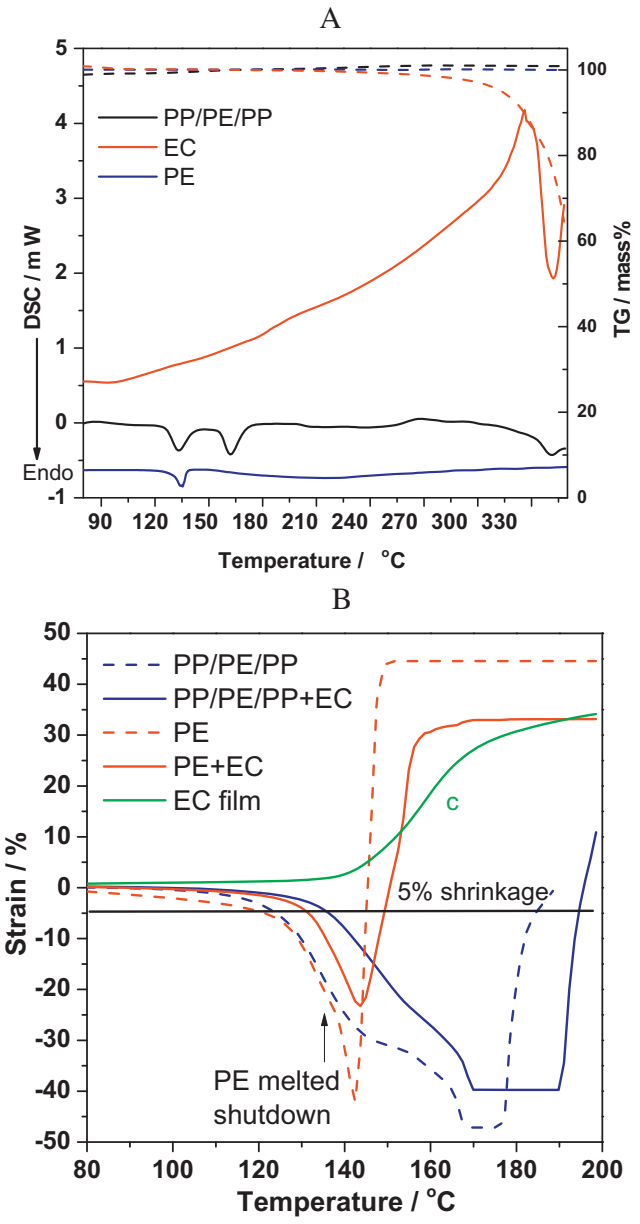


Fig. 2. (A) DSC and TG curves of EC, PE separator and PP/PE/PP separator; (B) thermomechanical behavior of separators and EC membrane.

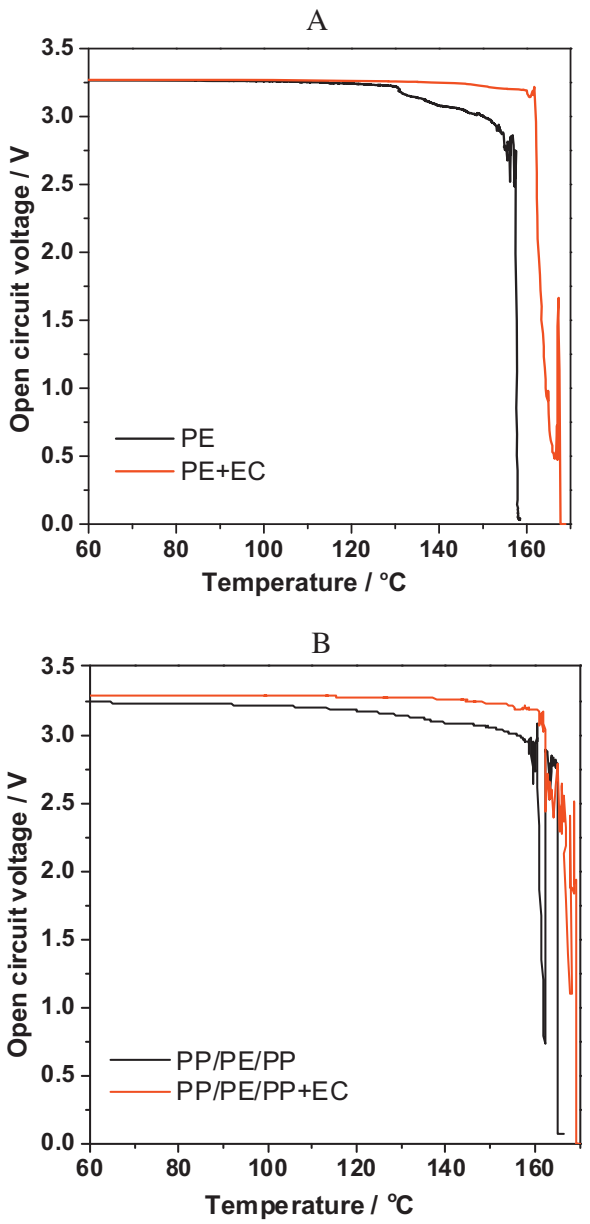


Fig. 3. Open-circuit voltage (OCV) of the cell as a function of temperature: (A) PE and PE + EC; (B) PP/PE/PP and PP/PE/PP + EC.

To perform the high temperature test, a full cell was assembled by sandwiching the separator between an MCMB (Mesophase Carbon Micro Beads) anode and an $LiFePO_4$ cathode and then activated by filling liquid electrolyte. Then the cell was sealed in a CR2032 shell by using a sealing machine (MSK-110, MTI Corp) under the pressure of 50 kg cm^{-2}. All the cells were charged to 50% state of charge (SOC) with battery test equipment (CT2001A, LAND Electronics) after cycled for 100 times at 0.5 C and were then left at OCV condition for 24 h. They were heated in a heating mantle from room temperature to the point at which the OCV drops to zero. The temperature was measured with a thermometer (YC-727UD, Tenmars) by attaching the thermocouple to the cell surface, and was increased by 10 °C min^{-1}. The OCV was measured using an electrochemical workstation (CHI604D, CH Instruments).

2.2.3. Electrochemical measurements

The separators were fully soaked in a liquid electrolyte in an Ar-filled glove box. The electrolyte contained 1 M LiPF6 in ethylene carbonate/dimethyl carbonate (=1/1, v/v). The soaked separators were sandwiched between two stainless steel electrodes and assembled into a tightly sealed test cell. The ionic conductivity at different temperatures was investigated by an AC impedance analysis using an electrochemical workstation over the frequency range of 0.01–10^{6}Hz. It was calculated with the following Eq. (1):

$$\sigma = \frac{d}{RS} \tag{1}$$

where σ is the ionic conductivity, d is the thickness of the separator, R is the bulk resistance, and S is the area of the electrode. In this experiment, the area of the electrode is 1.86 cm^2.

The separators for the electrochemical stability measurement were sandwiched between lithium metal and stainless steel electrodes in a test cell. Then the electrochemical stability was determined by using liner sweep voltammetry from 2.5 V to 5.5 V at 2 mV s^{-1}.

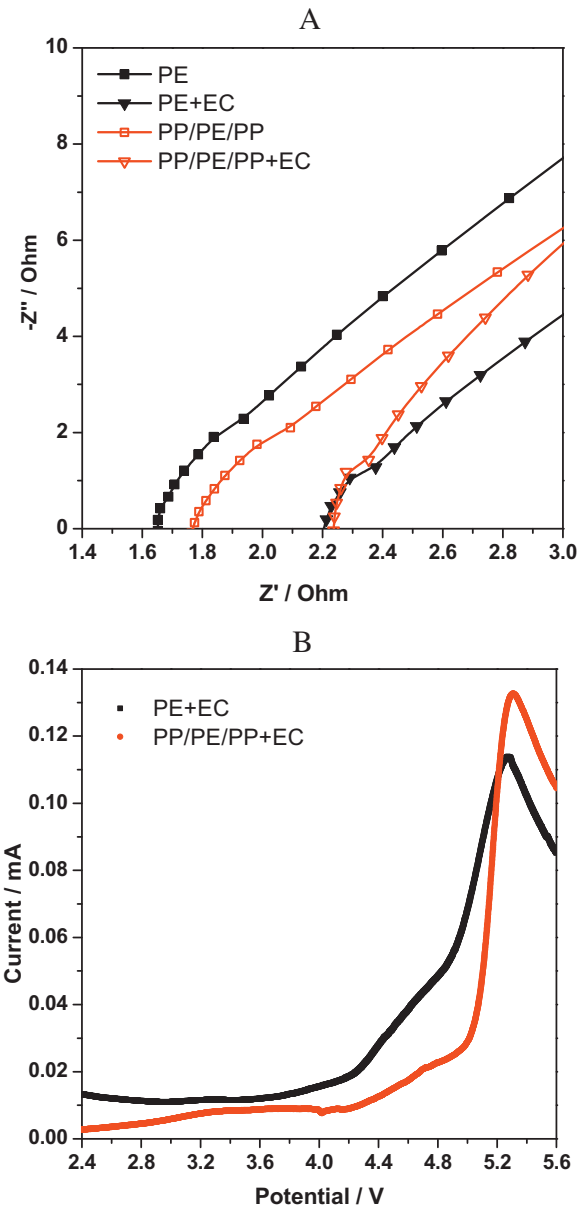


Fig. 4. (A) The AC impedance spectra of symmetric cells SS/separator/SS with different separators; (B) liner sweep voltammetry of the coated separators.

The cyclability tests of cells were performed using battery test equipment. A full cell was assembled by sandwiching the separator between an MCMB anode and an $LiFePO_4$ cathode and then activated by filling liquid electrolyte. The cells were cycled under a voltage range of 2.5–3.8 V and at a fixed charge/discharge current density of 0.5 C.

3. Results and discussion

3.1. Membrane characteristics of coated separators

SEM images of the surfaces for coated separators and uncoated ones are shown in Fig. 1. Both the commercialized PE separator and PP/PE/PP separator have porous structures with pore sizes of approximately 0.1–0.2 μm, as shown in Fig. 1(A1) and (B1). For convenience, the PE separator and trilayer PP/PE/PP separator were named as "PE" and "PP/PE/PP" respectively in figures, and after coating they were named as "PE + EC" and "PP/PE/PP + EC". After coating with EC, the surfaces of PE and PP/PE/PP separators were covered with highly porous EC layers, with the pore diameter of 2–5 μm and 5–10 μm, respectively (Fig. 1(A2)–(B2)). The pores in EC layer are resulted from the removal of PVP, which are interconnected and could facilitate the permeation and spreading of liquid electrolyte in separators.

3.2. Thermal properties

Separator shutdown is a useful mechanism to prevent thermal runaway reactions in Li-ion batteries. It usually happens at the melting temperature of the polymer which causes the collapse of pores, turning the ionically conductive polymer film into a non-porous insulating layer between the electrodes (Venugopal, Moore, Howard, & Pendalwar, 1999). Fig. 2A shows the TGA and DSC curves of commercialized separators. The single PE separator melted at around 135 °C, while the trilayer separator maintained the melting points of 132 °C for its PE layer and 162 °C for PP layer. Therefore, both of the single PE and trilayer separator have shutdown temperatures between 130 °C and 140 °C, and this shutdown function can still be kept even after coating with EC since the melting point is the intrinsic property of polymer. The thermal property of EC is also presented in Fig. 2A, which shows the decomposition temperature above 300 °C (3% mass loss), making it thermally stable and suitable for coating. There are no significant changes found in DSC curves before 300 °C, however, according to the TMA test the softening point of EC is around 140 °C as shown in Fig. 2B(c).

In order to avoid contact between positive and negative electrode, separators must not shrink significantly under increasing temperature, especially before the shutdown. Besides that, separators with good mechanical integrity at high temperature can provide a greater margin of safety for lithium-ion cells (Arora & Zhang, 2004). In the TMA test, the separator is held under constant load with increasing temperature. The elongation of separator versus temperature is measured to determine its thermal shrinkage and mechanical integrity. The TMA curves of separators are shown in Fig. 2B. We only test the shrinkage on axial direction because PE separator is isotropic and shows no difference between axial and transverse direction, and for trilayer separator the shrinkage in the transverse direction is quite low (Love, 2011). As can be seen in the figure, the thermal stability of commercial separators has been greatly improved after coating. For single PE separator, the temperature for 5% shrinkage was delayed from 122 °C to 132 °C, the shrinkage at shutdown point was decreased from 20% to 9%, maximum shrinkage was reduced by 19%, from 42% to 23%. Therefore, by coating with EC, the shrinkage of PE can be effectively delayed and reduced, which contribute to a safer lithium-ion battery. The same effect can also be observed for trilayer PP/PE/PP separator. Such a result can be explained by the zero thermal shrinkage of the EC layer (Fig. 2B(c)), which sticks to the surface of commercial separators and thus inhibit their thermal shrinkage.

To further present the improvement of thermal stability brought by the coating process, the open-circuit voltage (OCV) of the cell as a function of temperature was studied (Fig. 3). Before coating with EC, the OCV of the cell started to decline at 130 °C and drops to zero at 158 °C (Fig. 3A), indicating the happening of an internal short-circuit caused by the formation of pinholes and separator meltdown, respectively. However, the OCV of the cell with coated PE separator maintained same as the temperature increased to 160 °C. It should be attributed to the fact that the pinholes formed in the PE layer were covered by EC layer and consequently could not expand large enough to create a short circuit (Uchida, Ishikawa, Mohamedi, & Umeda, 2003). Apart from that, the temperature at which OCV drops to zero was also increased to 168 °C and could be caused by the increased meltdown temperature and lower thermal shrinkage of coated separator. The same trend was observed

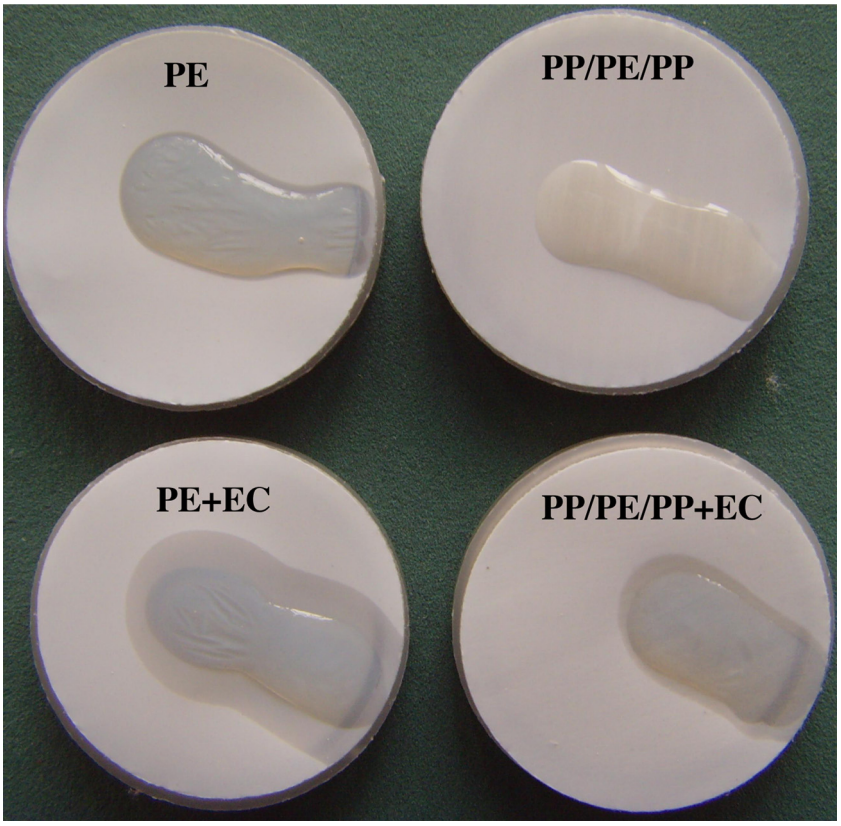


Fig. 5. Comparison of the liquid electrolyte wettability between different separators.

for trilayer separator as well (Fig. 3B), in which the coated trilayer separator performed better in keeping the OCV from dropping. For trilayer separators, the presence of the higher melting PP layer provides the separator with good mechanical properties above the shutdown temperature, thereby lead to higher short circuit temperature (Venugopal, 2001).

3.3. Ionic conductivity, electrochemical stability and wettability

Fig. 4A illustrates the AC impedance spectra of the cells with coated and uncoated separators. As is shown in the figure, the resistance of both PE and PP/PE/PP separator slightly increased after coating, which means the coating of porous EC layer does not hinder the lithium ion transfer too much. After coating, the thickness of PE separator increased from 22 μm to 28 μm, and the thickness of PP/PE/PP separator increased from 25 μm to 31 μm. Thus, considering the augmentation in thickness, the ionic conductivity has barely changed. According to Eq. (1), the ionic conductivity of PE decreased from about 0.72 to 0.68 mS cm^{-1}, while that of PP/PE/PP decreased from 0.76 to 0.74 mS cm^{-1}.

The electrochemical stability window of the coated separator was evaluated by linear sweep voltammetry. Fig. 4B shows that a very weak back-ground current was measured before 4.3 V, followed by a considerable increase in current flow indicating the onset of electrochemical decomposition. This result demonstrates the coated separator is stable enough to endure the operating voltage of the battery system.

The electrolyte wettability of separators is essential for cycle performance of lithium-ion battery (Zhang et al., 2013). The electrolyte wettability of coated and uncoated separator is shown in Fig. 5. When liquid electrolyte was dropped on the surface of separators, it formed a bead on the trilayer PP/PE/PP separator but quickly wetted three others. After 20 min, the droplets were easily spread into a larger area for the coated ones, while the uncoated separators remained same. This indicates that the coated separators have better liquid electrolyte affinity than uncoated ones. The poor wettability of PP/PE/PP separator can be explained by its hydrophobility (Huang, 2012). The improved wettability of the coated separator is possibly due to the relatively high polarity and the well-connected pores of EC layer, which may facilitate the intrusion of the liquid electrolyte into the electrolyte-philic pores (Choi & Lee, 2011).

3.4. Electrochemical performance

Fig. 6 compared the discharge capacity versus cycle number of full cells using coated polyolefin separators and the pristine separators respectively. It can be clearly seen that the cell containing coated PE separator initially shows lower capacity than uncoated ones but gradually catch up with the PE system at 30th cycle (Fig. 6A). At the end, the cell with coated PE separator presents lower discharge capacity than the one with pristine PE separator. Given that the two of the separators have nearly the same electrolyte wettability, the slight difference in discharge capacity might be due to impedance of EC layer on the diffusion of lithium ions to some extent.

In contrast, the cycling performance of the cell with coated trilayer separator greatly outperformed the cell with uncoated separator (Fig. 6B). The cell with the EC coated separator has an initial capacity similar to the cell with the uncoated separator, but the former one retained 99% of the starting discharge capacity compared to 28% of the latter at the 100th cycle. The bad cycle performance of the pristine trilayer separator was primarily attributed to its poor electrolyte wettability, since it cannot hold enough amount of liquid electrolyte which will be gradually consumed in the formation of the solid electrolyte interface (SEI) film and in the cycling

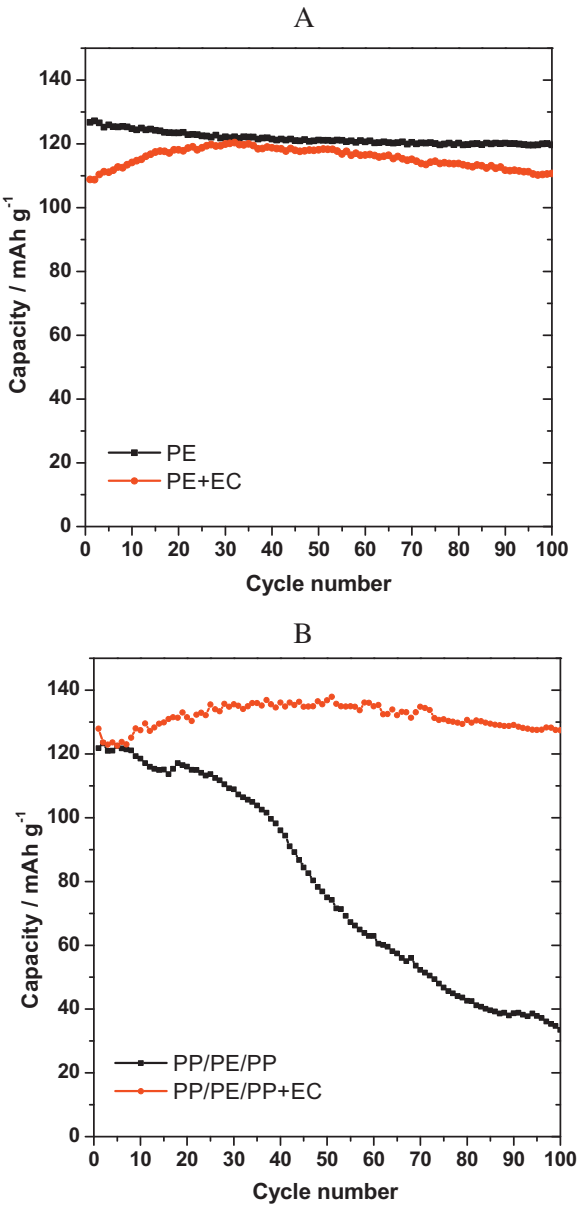


Fig. 6. Cycle performance of cells with different separators: (A) PE and PE + EC; (B) PP/PE/PP and PP/PE/PP + EC.

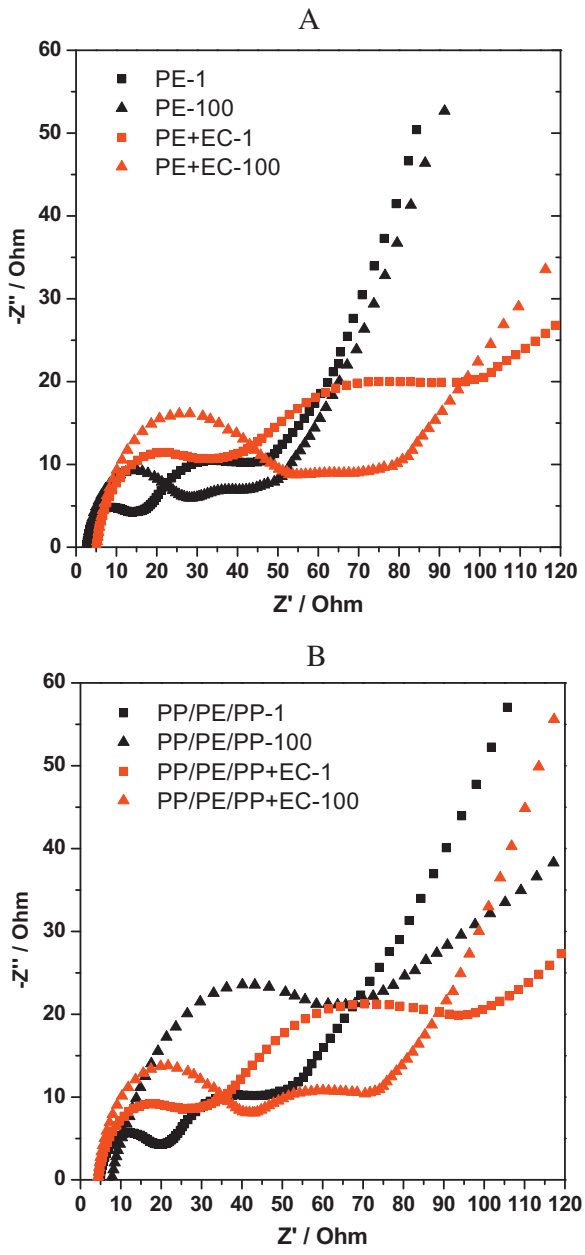
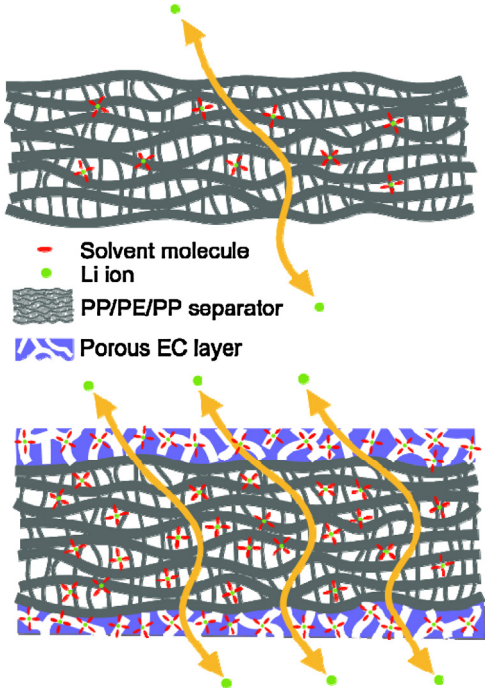


Fig. 7. Variation in AC impedance spectra (1st cycle/100th cycle) of cells assembled with different separators: (A) PE and PE + EC; (B) PP/PE/PP and PP/PE/PP + EC.

process, leading to the occurrence of "electrolyte scarcity" (Li & Gao, 2010). Subsequently, the cell with trilayer separator experienced a continuing increase in resistance, resulted in larger polarization and declining capacity. The fast fading capacity of pristine separator caused by poor electrolyte wettability was also observed by other researchers, in which the capacity retention was only 28.5% in the minimum (Cho et al., 2011; Fang et al., 2011; Li & Gao, 2010). The EC layer improves the wettability of the separator with its better affinity to polar organic electrolytes and can hold more electrolytes which are essential for good capacity retention. As shown in Scheme 1, the coating process can ensure the good ionic conductivity of trilayer separators for the much more abundant liquid electrolyte that is held in EC layer after cycling for 100 times. An interesting feature of the cycling profile in Fig. 6A and B for cells with coated separator is an upturn that happened between the 1st and 30th cycle. This unique self-healing effect has also been reported in previous studies and seems to have no relation with the stabilization of the solid electrolyte interface (Fang et al., 2011).

The conclusion can be further confirmed by analyzing the AC impedance spectra of cells after the 1st and 100th cycle. As shown in Fig. 7A and B, the semicircle of impedance spectra at the high frequency range represents the resistance of surface films on electrode materials and the semicircle observed at the medium-to-low frequency region can be ascribed to the charge transfer resistance between electrode materials and liquid electrolyte (Lee, Won, Kim, Kim, & Lee, 2012). The intercepts of the impedance spectra at the real axis represent the electrolyte bulk resistances (Rb) (Zhang, Sun, Hu, Yuan, & Chen, 2012). For PE separator, the cell with coated and uncoated separator showed similar growth in the impedance after 100 cycles, and the semicircles at medium frequency are all compressed into a smaller one, reflecting the stabilized charge transfer between electrodes and liquid electrolyte (Fig. 7A). For trilayer separator, the cell with uncoated separator experienced larger impedance growth than that of the coated one after cycled for 100 times. The bulk resistance of the pristine trilayer separator



Scheme 1. Schematic of a better cycling performance due to the improvement in liquid electrolyte retention.

was also increased from 4.8 Ω to 7.8 Ω, while that of coated separator remained the same (Fig. 7B). The great increase in impedance can account for its bad cycle performance.

4. Conclusion

New separators were prepared by coating commercialized separators with ethylcellulose using a simple dipping and extracting process. It is found that for both PE separator and trilayer PP/PE/PP separator, the existing of EC layer can effectively improve the thermal stability and electrolyte wettability. Cells with these coated separators show better performance in high temperature and cycling test.

Acknowledgments

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References

Arora, P., & Zhang, Z. M. (2004). Battery separators. *Chemical Reviews*, *104*, 4419–4462.

Balakrishnan, P. G., Ramesh, R., & Kumar, T. P. (2006). Safety mechanisms in lithium-ion batteries. *Journal of Power Sources*, *155*(2), 401–414.

Cho, J.-H., Park, J.-H., Kim, J. H., & Lee, S.-Y. (2011). Facile fabrication of nanoporous composite separator membranes for lithium-ion batteries: Poly(methyl methacrylate) colloidal particles-embedded nonwoven poly(ethylene terephthalate). *Journal of Materials Chemistry*, *21*(22), 8192–8198.

Choi, E. S., & Lee, S. Y. (2011). Particle size-dependent, tunable porous structure of a SiO2/poly(vinylidene fluoride-hexafluoropropylene)-coated poly(ethylene terephthalate) nonwoven composite separator for a lithium-ion battery. *Journal of Materials Chemistry*, *21*(38), 14747–14754.

Chun, S.-J., Choi, E.-S., Lee, E.-H., Kim, J. H., Lee, S.-Y., & Lee, S.-Y. (2012). Eco-friendly cellulose nanofiber paper-derived separator membranes featuring tunable nanoporous network channels for lithium-ion batteries. *Journal of Materials Chemistry*, *22*(32), 16618–16626.

Fang, J., Kelarakis, A., Lin, Y.-W., Kang, C.-Y., Yang, M.-H., Cheng, C.-L., et al. (2011). Nanoparticle-coated separators for lithium-ion batteries with advanced electrochemical performance. *Physical Chemistry Chemical Physics*, *13*(32), 14457–14461.

Fu, D., Luan, B., Argue, S., Bureau, M. N., & Davidson, I. J. (2012). Nano SiO2 particle formation and deposition on polypropylene separators for lithium-ion batteries. *Journal of Power Sources*, *206*, 325–333.

Goodenough, J. B., & Park, K.-S. (2013). The Li-ion rechargeable battery: A perspective. *Journal of the American Chemical Society*, *135*(4), 1167–1176.

Hao, J., Lei, G., Li, Z., Wu, L., Xiao, Q., & Wang, L. (2013). A novel polyethylene terephthalate nonwoven separator based on electrospinning technique for lithium ion battery. *Journal of Membrane Science*, *428*, 11–16.

Huang, X. (2012). A lithium-ion battery separator prepared using a phase inversion process. *Journal of Power Sources*, *216*, 216–221.

Huang, X., & Hitt, J. (2013). Lithium ion battery separators: Development and performance characterization of a composite membrane. *Journal of Membrane Science*, *425*, 163–168.

Jhu, C.-Y., Wang, Y.-W., Wen, C.-Y., & Shu, C.-M. (2012). Thermal runaway potential of LiCoO2 and Li(Ni1/3Co1/3Mn1/3)O-2 batteries determined with adiabatic calorimetry methodology. *Applied Energy*, *100*, 127–131.

Jung, Y. S., Cavanagh, A. S., Gedvilas, L., Widjonarko, N. E., Scott, I. D., Lee, S.-H., et al. (2012). Improved functionality of lithium-ion batteries enabled by atomic layer deposition on the porous microstructure of polymer separators and coating electrodes. *Advanced Energy Materials*, *2*(8), 1022–1027.

Lee, J.-R., Won, J.-H., Kim, J. H., Kim, K. J., & Lee, S.-Y. (2012). Evaporation-induced self-assembled silica colloidal particle-assisted nanoporous structural evolution of poly(ethylene terephthalate) nonwoven composite separators for high-safety/high-rate lithium-ion batteries. *Journal of Power Sources*, *216*, 42–47.

Li, H., Ma, X.-T., Shi, J.-L., Yao, Z.-K., Zhu, B.-K., & Zhu, L.-P. (2011). Preparation and properties of poly(ethylene oxide) gel filled polypropylene separators and their corresponding gel polymer electrolytes for Li-ion batteries. *Electrochimica Acta*, *56*(6), 2641–2647.

Li, S., & Gao, K. (2010). The study on methyl methacrylate graft-copolymerized composite separator prepared by pre-irradiation method for Li-ion batteries. *Surface & Coatings Technology*, *204*(16–17), 2822–2828.

Liao, Y. H., Li, X. P., Fu, C. H., Xu, R., Zhou, L., Tan, C. L., et al. (2011). Polypropylene-supported and nano-Al2O3 doped poly(ethylene oxide)-poly(vinylidene fluoride-hexafluoropropylene)-based gel electrolyte for lithium ion batteries. *Journal of Power Sources*, *196*(4), 2115–2121.

Liu, J., Li, W., Zuo, X., Liu, S., & Li, Z. (2013). Polyethylene-supported polyvinylidene fluoride-cellulose acetate butyrate blended polymer electrolyte for lithium ion battery. *Journal of Power Sources*, *226*, 101–106.

Love, C. T. (2011). Thermomechanical analysis and durability of commercial microporous polymer Li-ion battery separators. *Journal of Power Sources*, *196*(5), 2905–2912.

Miao, Y.-E., Zhu, G.-N., Hou, H., Xia, Y.-Y., & Liu, T. (2013). Electrospun polyimide nanofiber-based nonwoven separators for lithium-ion batteries. *Journal of Power Sources*, *226*, 82–86.

Muschert, S., Siepmann, F., Cuppok, Y., Leclercq, B., Carlin, B., & Siepmann, J. (2009). Improved long term stability of aqueous ethylcellulose film coatings: Importance of the type of drug and starter core. *International Journal of Pharmaceutics*, *368*(1–2), 138–145.

Ryou, M.-H., Lee, Y. M., Park, J.-K., & Choi, J. W. (2011). Mussel-inspired polydopamine-treated polyethylene separators for high-power Li-ion batteries. *Advanced Materials*, *23*(27), 3066–3070.

Song, K. W., & Kim, C. K. (2010). Coating with macroporous polyarylate via a non-solvent induced phase separation process for enhancement of polyethylene separator thermal stability. *Journal of Membrane Science*, *352*(1–2), 239–246.

Uchida, I., Ishikawa, H., Mohamedi, M., & Umeda, M. (2003). AC-impedance measurements during thermal runaway process in several lithium/polymer batteries. *Journal of Power Sources*, *119*, 821–825.

Venugopal, G. (2001). Characterization of thermal cut-off mechanisms in prismatic lithium-ion batteries. *Journal of Power Sources*, *101*(2), 231–237.

Venugopal, G., Moore, J., Howard, J., & Pendalwar, S. (1999). Characterization of microporous separators for lithium-ion batteries. *Journal of Power Sources*, *77*(1), 34–41.

Zhang, J., Liu, Z., Kong, Q., Zhang, C., Pang, S., Yue, L., et al. (2013). Renewable and superior thermal-resistant cellulose-based composite nonwoven as lithium-ion battery separator. *ACS Applied Materials & Interfaces*, *5*(1), 128–134.

Zhang, L. C., Sun, X., Hu, Z., Yuan, C. C., & Chen, C. H. (2012). Rice paper as a separator membrane in lithium-ion batteries. *Journal of Power Sources*, *204*, 149–154.

Zhu, Y., Wang, F., Liu, L., Xiao, S., Chang, Z., & Wu, Y. (2013). Composite of a nonwoven fabric with poly(vinylidene fluoride) as a gel membrane of high safety for lithium ion battery. *Energy & Environmental Science*, *6*(2), 618–624.